Comparison of selected optical properties of oxyfluoride glass fibers doped with Er^{3+} and co-doped with Er^{3+} Yb^{3+}

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Abstract The method of manufacturing and spectroscopic evaluation of the Er^{3+} ions doped and Er^{3+} – Yb^{3+} co-doped SiO_2 – Al_2O_3 – Na_2CO_3 – CaO – PbO – PbF_2 oxyfluoride glass fibers is presented in the paper. Both optically active elements erbium and ytterbium were introduced into the batch in the form of fluorides. The X-ray diffraction (XRD) technique was applied at each stage of fibers manufacturing in order to control an amorphous structure of the preforms and fibers. Optical studies of glass preforms and fibers (reflection/transmission, absorption, emission, and excited state absorption (ESA)) were directed to examine their suitability as fiber amplifiers at 1.55 μm band.

1 Introduction

Search for novel glass materials as hosts for rare-earth doped fiber amplifiers and lasers is still an attractive subject [1–3]. The comparison of oxide and fluoride glass features shows that each of them has some advantages and disadvantages. Oxide glasses are characterized by relatively good chemical and optical stability, but suffer from rather large

maximum phonon energies promoting non-radiative transitions via multi-phonon relaxation, but first of all, from the OH^- groups, since their absorption covers substantial range around 1400 nm. On the other hand, fluoride glasses have considerably lower maximum phonon energies, which is an undoubted advantage, but they are more expensive due to their rather complex technology and very vulnerable to possible contamination by the oxygen ions during melting. To find a reasonable compromise between the features mentioned above there are some attempts to search candidates among oxyfluoride glasses and glass ceramics [4–6].

Many studies were dedicated to the oxyfluoride glasses and glass ceramics in the following systems: SiO_2 – PbO – PbF_2 [7–9], SiO_2 – CdF_2 – PbF_2 [10–12], GeO_2 – PbO – PbF_2 [13–15], however in the papers mentioned above only the bulk form of glass materials was considered but not fibers. Hence, the manufacturing and examination of the oxyfluoride glass fibers doped with rare-earth ions seem to be a serious challenge. In the present paper the manufacturing of the oxyfluoride glass fibers doped with Er^{3+} ions and co-doped with Er^{3+} and Yb^{3+} ions has been briefly described. The amorphous structure of obtained glass preforms as well as glass fibers was controlled by XRD technique whereas a refraction index has been estimated by reflection/transmission measurements. The suitability of invented glasses (fibers) for optical amplifiers is discussed also from the point of view of their absorption (GSA, ESA) and emission properties. It is well known that the wavelength of 1.55 μm corresponding to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition in Er^{3+} ions is used in telecommunication. The upper level can be pumped via $^4\text{I}_{11/2}$ level by commercially available diodes, however, absorption into the $^4\text{I}_{11/2}$ level of erbium ions is not very high. For that reason (sufficient pumping rate) ytterbium co-doping can be applied in order to enhance the material absorption cross-section at about 975 nm. Then in co-doped

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material an efficient Yb–Er energy transfer can elevate the population of the Er^{3+} states. On the other hand, some authors [16] report undesirable visible upconversion of erbium ions excited indirectly resulting in a reduction of the quantum efficiency in the infrared. Such an effect has been observed by them, however, in germanate glasses but not in silicate oxyfluoride.

2 Experimental

Preparation of erbium doped and erbium-ytterbium co-doped oxyfluoride glass fibers

2.1 Glass preform fabrication

Oxyfluoride glasses of the following compositions $48\text{SiO}_2-11\text{Al}_2\text{O}_3-7\text{Na}_2\text{CO}_3-10\text{CaO}-10\text{PbO}-11\text{PbF}_2-3\text{ErF}_3$ and $48\text{SiO}_2-11\text{Al}_2\text{O}_3-7\text{Na}_2\text{CO}_3-10\text{CaO}-10\text{PbO}-10\text{PbF}_2-3\text{YbF}_3-1\text{ErF}_3$ (in molar %) were fabricated from high purity commercial chemicals (Sigma-Aldrich). Batches were thoroughly mixed in an agate mortar in argon atmosphere, put in a corundum crucible and melted at 1450°C for 1.5 h in air. The liquid melts were poured into a brass mold and glassy rods (preforms) of approximate dimensions of $5 \times 5 \times 50$ mm were obtained. Transparent glass preforms were annealed for several hours below glass transition temperature T_g and then cooled passively. Differential thermal analysis (DTA) of glass preforms was employed (symmetric Setaram analyzer at the heating rate of $10^\circ\text{C}/\text{min}$ in helium) in order to determine the glass transition temperature T_g , the crystallization onset T_x and the crystallization maximum rate temperature T_p (see an example in Fig. 1), which allowed one to estimate the fiber drawing temperature.

Fig. 2 Optical and SEM micrographs (secondary electron image) of various diameter glass fibers

2.2 Glass fibers drawing

The fabricated glass preforms were drawn into glass fibers using the mini-tower. The preform was mounted in the head at the top of the drawing-tower then moved down with a controlled speed into the vertical furnace heated to the glass softening point. The drawing process was started and continued at the temperature range of $720-740^\circ\text{C}$. The fibers of different thickness (about $30\text{ }\mu\text{m}$ and about $500\text{ }\mu\text{m}$) have been drawn (Fig. 2). Thick fibers were provided for structure examination and thin fibers for optical measurements.

X-ray diffraction (XRD) measurements (X-Pert Philips diffractometer equipped with curved graphite monochromator, $\text{Cu K}\alpha$ radiation) confirmed amorphous structure for both fibers compositions (see X-ray diffraction patterns of glass fibers in Fig. 3).

Fig. 1 DTA plot of oxyfluoride glass preform. Indicated characteristic temperatures: glass transition T_g , crystallization onset T_x , crystallization maximum rate T_p

Fig. 3 XRD patterns of erbium doped and erbium-ytterbium co-doped glass fibers. The broad band at about 28° is typical for amorphous structures

3 Optical evaluation

3.1 Refractive index measurements

The refractive index of studied glasses has been established by reflection/transmission measurements of perpendicular beam in the wavelength range of 450–850 nm and subsequent extrapolation to the range of 850–1500 nm by the least squares fit to the Cauchy dispersion relation (see Fig. 4). Its value for erbium doped glass has been found to be 1.507 for $\lambda = 1500$ nm.

3.2 Absorption and emission spectra

Absorption spectra of both materials are shown in Fig. 5 along with assignments of the transitions. The spectra reveal features typical for erbium and erbium/ytterbium ions in glassy host. One may note an interesting competition between $^2\text{H}_{11/2}$ and $^4\text{I}_{11/2}$ states without and with ytterbium content. Significant growth of the absorption at 975 nm in the ytterbium co-doped sample suggests superposition of direct $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ transition in the Er^{3+} ions and the Yb^{3+} excitation from $^2\text{F}_{7/2}$ to the $^2\text{F}_{5/2}$ state with domination of the latter. An exact match of both peaks at the same wavelength ~ 975.2 nm is worth noting.

Emission spectra have been registered with 980 nm excitation (semiconductor laser) and are depicted in Fig. 6. Upper two spectra are Stokes emission of Er and Er–Yb doped samples, respectively, whereas lower spectra show the up-converted emission. According to the latter it is very interesting that at the same measurement sensibility as in Fig. 6d, we were not able to record any upconverted emission for erbium doped sample. This is certainly associated with an absence of Yb^{3+} co-dopant in this case as well as with high Er^{3+} concentration. However, changing the sensitivity it can

Fig. 4 Refractive index of Er doped oxyfluoride glass. Experimental plot and extrapolation according to the Cauchy expression

Fig. 5 Absorption spectra of Er^{3+} and Er^{3+} , Yb^{3+} activated fibers

be managed to measure the emission spectrum as shown in Fig. 6c (noisy spectrum proves the very low emission intensity). The peak around 590 nm appears likely due to the sodium content (see chapter on preparation).

3.3 Excited State Absorption, methodology

Examination of the excited state absorption (ESA) seems to be a key issue in searching for novel materials for doped optical fibers addressed to the fiber amplifier applications.

Fig. 6 Stokes- and anti-Stokes emission spectra of Er^{3+} and Er^{3+} , Yb^{3+} activated fibers. All the denoted transitions occur to the ground $^4\text{I}_{15/2}$ state. The excitation line was 980 nm

The measurements of the ESA spectra in bulk materials are well developed and reported many times [17–21]. However, in case of optical fibers the ESA data are presented not very frequently. Recently the previously utilized experimental setup serving to the measurements of the ESA spectra in bulks has been modified to the form suitable for fibers. The modified setup is depicted in Fig. 7.

When measuring the ESA spectra one can realize that recording the transmittances of the probe beam passing through the pumped (T_p) and unpumped (T_u) medium we will see not only the ESA features but also stimulated emission (SE, gain) and ground state absorption (GSA) in the form of so called GSA bleaching. All of these features are seen in the transmittance of the excited state (T_{ES}) which is expressed as follows:

$$T_{\text{ES}} = \frac{T_p}{T_u} = \frac{I_p}{I_u} = \frac{I \pm \Delta I}{I} = 1 \pm \frac{\Delta I}{I} = \exp\{(\sigma_{\text{SE}} - \sigma_{\text{ESA}} + \sigma_{\text{GSA}})N^*L\} \quad (1)$$

Here I_p , $I_u = I$ are the probe beam intensities measured after passing through the pumped and unpumped medium; σ_{SE} , σ_{ESA} , σ_{GSA} are the SE, ESA and GSA cross-sections, respectively; N^* is the excited state population, and L is the sample length. Note that the σ_{GSA} has in (1) the same sign as σ_{SE} so that it can imitate the gain. This bleaching feature should be taken into account when interpreting the spectra. In the case of RE^{3+} ions in the fiber, when we deal usually with more than one state excited, the relative change of the signal intensity when the medium is excited: $\pm \Delta I/I$ should be expressed in this way [22, 23]:

$$\frac{\Delta I(\lambda)}{I(\lambda)} = L \left(N^* \sigma_{\text{GSA}}(\lambda) + \sum_i N_i (\sigma_{\text{SE}_i}(\lambda) - \sigma_{\text{ESA}_i}(\lambda)) \right) \quad (2)$$

where N^* is the total excited states population and N_i is the i th excited state population ($\sum N_i = N^*$). Equation (2) is approximated (it has no exponential character) but in the

Fig. 7 Experimental setup used to the measurements of the ESA spectra **Fig. 8** $\Delta I/I$ spectra of Er^{3+} and Er^{3+} , Yb^{3+} activated fibers excited by 488 nm line, registered in two spectral ranges: 550–900 nm and 900–1800 nm

condition of experiment, with relatively small fraction of excited ions (N^*) such an approximation works very well. In the real experiment we can simultaneously see all the

features involved in (2), and then the ESA features (e.g. peaks) are negative according to “zero line” on the spectrum whereas SE and GSA bleaching are positive.

The experimental setup being a modified version of that used previously, is presented in Fig. 7. The key modification was the employment of an additional optics designed for introduction of the signal into the fiber and its recovery at the output. A CW laser (e.g. Ar ion laser or diode laser) and halogen lamp serve as sources of excitation (pump) and probe beams, respectively. In the detector branch a 0.4 m monochromator was used with amplified PIN photodiodes (DET36A or DET410, ThorLabs) (PD) at the output. The PD signal was analysed by a cascade of two lock-in amplifiers (Signal Recovery 7265), each controlled by a chopper of different reference frequency, usually of the order of 1 kHz (for the probe beam) and 10 Hz (for the pump). The detailed account of the system is given in [23, 24]. The enormous sensitivity of the system is worth noting: dealing with $(\Delta I/I)$ as small as $\sim 10^{-5}$ it is still possible to record smooth and readable spectra. In can be noted in the mentioned context that the spectra described below are expressed as $A * \Delta I/I$ in Figs. 8 and 9, where A is an ampli-

Using two types of detectors at the monochromator output the $\Delta I/I$ spectra in two spectral ranges can be recorded: 550–900 nm and 900–1800 nm. Because of rather high concentration of erbium (high for fibers), fiber samples of the reduced length of 15 and 12 mm were used. The results for 488 nm excitation are shown in Fig. 8. First of all it is seen that Er–Yb doped fiber reveals more distinct spectra. This can be due to the different concentration of erbium ions in

Fig. 10 Model explaining possible upconversion routes when the Er^{3+} , Yb^{3+} activated sample is excited by the 980 nm laser line. ETU: energy transfer upconversion

the examined samples, which is 3% for Er doped fiber and 1% for Er–Yb co-doped sample. At any rate, quality of the $\Delta I/I$ spectra is much better for the latter case. Looking at the Er doped fiber data we observe considerably larger values for $\Delta I/I$ than in Er–Yb co-doping case. This is due to higher excitation strength for larger concentration, than for smaller one in case of Er–Yb co-doping. On the other hand, because of higher ground state absorption due to higher doping concentration in the Er doped fiber, ΔI is divided by a smaller signal I , and therefore we obtain larger noise for $\Delta I/I$.

In Fig. 9 the equivalent set of $\Delta I/I$ spectra is presented but this time registered with the 980 nm excitation (semiconductor laser). The observations are here very similar to that described above, but the average quality of the spectra is better (see e.g. the case of Er^{3+} doped fiber in the range of 900–1800 nm). It seems that with 980 nm excitation we excite both ions: Er^{3+} into the $4I_{11/2}$ state and Yb^{3+} into the $2F_{5/2}$ state and then possible Yb–Er [25, 26] and Er–Er energy transfers probably accompanied by the ESA transitions [27], as illustrated in Fig. 10, cause a larger population of the excited states.

4 Conclusion

The Er doped and Er/Yb co-doped oxyfluoride glass fibers of desirable diameter were obtained as a result of appropriate selection of chemical composition and method of fabrication. DTA results allowed to determine the fiber drawing temperature. XRD measurements confirmed that the undesirable crystallization in the preforms and in glass fibers has

been avoided. The emission spectra reveal relatively easily upconverted luminescence for 980 nm excitation, as far as the Er^{3+} doped fiber is codoped with Yb^{3+} ions. According to the ESA/gain spectra measurements the substantial gain feature around 1600 nm is worthwhile to note and it is even more attractive as occurring for diode laser excitation (980 nm) more effectively than for Ar ion laser excitation. The better quality of the emission and ESA/gain spectra for the samples doped with $\text{Er}^{3+}/\text{Yb}^{3+}$ ions is surely connected with the lower erbium content in these samples and with higher population of the states responsible for both types of transition, due to the effective energy transfer from Yb^{3+} to Er^{3+} ions [25, 26].

All results seem to be a sufficient support for fabrication of optical fibers with reduced concentration of erbium and ytterbium ions (to avoid concentration quenching).

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